Further analysis of electronic states in the muffin-tin model of a disordered alloy

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Several new results on the evaluation of the spectral function \( A(k,E) \) and average density of states \( p(E) \) in a realistic model of a substitutional binary alloy are presented. This work is primarily concerned with the conditions under which a given approach can be relied upon to yield a non-negative spectrum. In the average t matrix and coherent-potential approximations, a link is established between the sign of \( A(k,E) \) and the Argand diagram for the energy-shell matrix elements \( \tau_e \) of the effective atomic scattering operators: If \( \tau_e \) lies within the unitarity circle, then \( A(k,E) > 0 \). The connection between this result and our earlier work on the optical theorem is shown to require a renormalization of certain free-electron singularities. Finally, an independent proof is outlined, based on the Lloyd equations, that the coherent potential density of states is always non-negative.

I. INTRODUCTION

In a disordered alloy, the average density of electronic states \( p(E) \) is obtained by integrating the spectral function \( A(k,E) \) over all momenta \( k \).\(^1\,2\) While both these quantities are, by definition, non-negative, approximate calculations in strong scattering systems often lead to negative results.\(^3\,4\) Accordingly, recent authors have considered the problem of classifying the analytic properties of alternate approximation schemes.\(^5\,6\) In the present paper, we consider several issues, all related to this general problem.

It is by now well known that the average t matrix (ATA) and coherent-potential (CPA) approximations are both constrained to yield non-negative spectral densities.\(^5\,7\) Unfortunately, extant proofs of these results are not very transparent nor are they formulated directly in terms of the quantities involved in the most accurate calculations of electronic states in substitutional alloys, namely those based on the muffin-tin model.\(^4\,10\) We show in Sec. II, however, that the final expressions for \( A(k,E) \) obtained in Ref. 6 have a simple interpretation in terms of the Argand diagram for the energy-shell matrix elements \( \tau_e = \tau_e' + i\tau_e'' \) of the effective atomic scattering operator. For a given partial wave index \( L \), if the plot of \( k\tau_e' \) vs \( k\tau_e'' \), as a function of the parameter \( k^2 = E \), lies within the unitarity circle, \( (k\tau_e')^2 + (k\tau_e'' + i)^2 < 1 \), then \( A(k,E) > 0 \). While previous authors\(^8\,12\) have discussed such plots in connection with both the ATA and the CPA, the relationship between these diagrams and the sign of the average spectrum has not previously been established.\(^13\) (Although we consider only the CPA in detail, analogous results for the ATA are easily derived.)

In applying the optical theorem to the multiple-scattering series,\(^6\) we showed that the various contributions to \( A(k,E) \) can be regrouped into a sequence \( S_n(k,E) \) of increasingly accurate non-negative terms. While \( S_n(k,E) \) is indeed non-negative for all \( E = E' + iE'' \) in the upper half plane, it turns out that certain contributions to \( S_n(k,E) \) are singular as \( E'' \rightarrow 0^+ \). Although the regrouping process employed in Ref. 6 is not unique, alternate rearrangements into non-negative terms are also expected to exhibit such singularities. [Technically, they arise because we are dealing with a perturbation series based on the (unrenormalized) free-electron Green's function.] In Sec. II C the origin of these singularities is discussed and it is shown that, once terms of all orders are properly summed, they are renormalized and no ambiguities arise in the interpretation of our final equations for \( A(k,E) \).

Finally, in Sec. III we consider the commonly employed formula\(^14\,15\) for the CPA density of states which is based on more general equations derived by Lloyd.\(^1\) Since these equations involve energy derivatives of both \( \tau_e \) and the Karrin-ga-Kohn-Rostoker (KKR) structure functions\(^15\) \( B_L \), they are more difficult to work with from a formal standpoint than the original multiple-scattering equations. We show, however, that the various components in this formula for \( p(E) \) can be written in a manifestly non-negative form. Once again the crucial property of the CPA is the fact that \( \tau_e \) lies inside the unitarity circle.

II. ARGAND DIAGRAMS AND SPECTRAL FUNCTIONS

A. General equations

In the muffin-tin model of the substitutional alloy \( \Lambda_1B_{1-} \), the disordered potential \( \bar{\Psi}(\bar{E}) \) is written as
a sum of \( N \) nonoverlapping spherically symmetric contributions \( \rho_{aa'}^{(BB)}(\mathbf{r}) \equiv \rho_{aa'}^{(BB)}(\mathbf{r} - \mathbf{R}_a) \), and \( \mathcal{U}(\mathbf{r}) \) is nonvanishing within a muffin-tin sphere of radius \( r_m \) surrounding each of the lattice sites \( \{ \mathbf{R}_a \} \) and is constant (by convention, zero) in the region between the spheres. The arrangement of the \( A \) and \( B \) atoms throughout the lattice is assumed to be random and their relative concentrations are \( x \) and \( y = (1 - x) \).

The equilibrium electronic properties of the alloy are calculated in terms of the average total scattering operator \( T(E) = \langle \mathcal{T}(E) \rangle = \langle \psi | (1 - \mathbf{G}_a(E)) \mathbf{U}^{-1} \rangle \). [Here the angular brackets indicate an ensemble average, \( E = E' + iE'' \) is a complex energy, \( \mathbf{G}_a(E) = (\mathbf{E} - \mathbf{H}_a)^{-1} \) is the free-electron resolvent operator, and \( \mathbf{H}_a = \mathbf{p}^2/2 \).] In summarizing the most important results of present interest, we note that \( A(k, E) \) can be expressed as (see Appendix A)

\[
\begin{align*}
A(k, E) &= \lim_{E' \to E} |E - k|^2 |E - k|^2 \langle \mathcal{E} | T(E) | \mathcal{E} \rangle \\
&= \langle \mathcal{E} | T(E) \delta(E - \mathbf{H}_a) T(E) | \mathcal{E} \rangle \\
&= \lim_{E' \to E} |E - k|^2 \langle \mathcal{E} | (\mathbf{r}^\mathbf{r} - \langle \mathbf{r}^\mathbf{r} \rangle) \delta(E - \mathbf{H}_a) \mathbf{r} \mathbf{r} \rangle \\
&= \lim_{E' \to E} |E - k|^2 \langle \mathcal{E} | T(E) | \mathcal{E} \rangle,
\end{align*}
\]

(2.1a)

where, on the right side of Eqs. (2.1), the operator \( \delta(E - \mathbf{H}_a) \) is to be interpreted as

\[
\tau \delta(E - \mathbf{H}_a) = E' + iE'' \cdot [E' - \mathbf{H}_a]^2 + (E'')^2 \cdot \mathbf{H}_a^{-1}.
\]

(2.2)

\( T(E) \) is most conveniently evaluated in terms of the effective atomic scattering matrices \( t_a(E) \) and the path operators \( Q_{aa'}(E) \):

\[
T = \sum_{aa'} Q_{aa'}(E),
\]

(2.3)

where

\[
Q_{aa'} = t_a \delta_{aa'} + t_a G_0 \sum_{\mathbf{R}_a} Q_{\mathbf{R}_a a'.}
\]

(2.4)

In the muffin-tin model the operators \( t_a \) are usually expressed in the angular representation. Of particular interest are the energy-shell matrix elements \( \tau_{L}(E) \) which are often written in terms of the auxiliary quantity \( \mathbf{C}_L(E) \) via

\[
\tau_{L}^{-1} = -\mathbf{C}_L + i \kappa.
\]

(2.5)

In the case of scattering by a real spherical potential, as \( E'' \to 0 \) we find \( C_L(E) \to \kappa \cos(\delta_L(E)) \), where \( \delta_L(E) \) is the usual phase shift. In the present case, however, \( C_L - iC_L' \) is \( E'' \to 0 \) and the sign of \( C_L' \) is related to the behavior of the Argand diagram for \( \tau_L \). For \( C_L' < 0 \) we will find bubbles outside the unitarity circle. Within the CPA, \( \tau_L(E) \) is determined by the equations

\[
\tau_L = \langle \tau_L \rangle - \langle \tau_L - \tau_L' \rangle B_L (\tau_L - \tau_L'),
\]

(2.6)

where \( \langle \tau_L \rangle = x \tau_L^A + y \tau_L^B \),

\[
B_L = \sum_{\mathbf{R}_a} B_L^{\mathbf{R}_a} \left( (1 - \tau \mathbf{B}_a)^{-1} \right)_{L \mathbf{R}_a},
\]

(2.7)

\( B_L^{\mathbf{R}_a} \) is the matrix of KKR structure functions and the \( \mathbf{F} \) sum runs over just the first Brillouin zone. It will prove convenient for us to rewrite (2.6) as

\[
\tau_L = \langle \tau_L \rangle + xy \Delta_L \Delta_L,
\]

(2.8)

where \( \Delta_L = \tau_L^A - \tau_L^B \) and \( f_L \) satisfies

\[
f_L = (1 + y \Delta_L) B_L (1 - x \Delta_L).
\]

(2.9)

Combining (2.8) with the identities

\[
\langle \tau_L \rangle'' = -\kappa(\langle \tau_L \rangle^2 + xy |\Delta_L|^2)
\]

(2.10)

and

\[
\Delta_L'' = -\kappa(\langle \tau_L \rangle^* \Delta_L + \Delta_L^* \langle \tau_L \rangle + (y - x) |\Delta_L|^2),
\]

(2.11)

we obtain

\[
\tau_L'' = -\kappa(\langle \tau_L \rangle^2 + xy |\Delta_L|^2 M_L),
\]

(2.12)

where

\[
M_L = 1 + (\langle \tau_L \rangle f_L - \kappa f_L^* + f_L^* \langle \tau_L \rangle)^* + (y - x)(\Delta_L f_L + f_L^* \Delta_L) - xy |\Delta_L|^2
\]

(2.13)

\[
= \frac{-|\tau_L|^2 (\kappa f_L^* / \kappa) - xy |\Delta_L|^2}{xy |\Delta_L|^2}.
\]

(2.14)

The inequality in (2.14) follows because the physical solutions of Eq. (2.6) are known to lie inside the unitarity circle. We consider next the bearing of this observation on the sign of the CPA spectrum.

### B. Proof that \( C_L''(E) \leq 0 \) implies \( A(k, E) \geq 0 \)

Combining Eq. (A2b) of Ref. 6 with (2.1a), the CPA spectral function may be written as

\[
A(k, E) = \lim_{E'' \to 0} \frac{\kappa \mathcal{F}}{N |E - k|^2} \sum_{\mathbf{R}_a} \left[ \mathcal{E} \left( 1 + \sum_{\mathbf{R}_a} Q_{\mathbf{R}_a a'} \Delta_{\mathbf{R}_a} m_{\mathbf{R}_a} \left( 1 + \sum_{\mathbf{R}_b} G_{\mathbf{R}_b} \right) \right) \mathcal{E} \right],
\]

(2.15)
Here
\[
\gamma_a = \left( 1 - [1 + (t_a)G_0 + (y - x)\Delta_a G_0] \sum_{\delta} \sigma_a G_0 \right)^{1/2}.
\]
(2.16b)
\[
\delta(E - H_0) \text{ is again to be understood as in Eq. (2.2),}
\]
\[
\langle t_a \rangle \equiv x t_a^A + y t_a^B, \quad \Delta_a \equiv t_a^A - t_a^B,
\]
\[
Q_a = \sum_{\alpha} q_{\alpha} t_{\alpha} + t_a G_0 \sum_{\delta} Q_\delta,
\]
(2.17)
and \( \sigma_a \) is the CP effective potential centered at the site \( \alpha \):
\[
t_{\alpha} = \sigma_a (1 - G_0 \sigma_a)^{-1}.
\]
(2.18)
In the angular representation the momentum matrix elements of \( Q_a \) take the form
\[
\langle \vec{k} | Q_a | \vec{k}' \rangle = e^{-i(\vec{k} \cdot \vec{k}')} \frac{4\pi^2}{\Omega} \sum_{L L'} Y_{L}^*(\vec{k}) Q_{L L'}(k, k') Y_{L'}(\vec{k}'),
\]
(2.19a)
where \( \Omega \) is the volume of the system and
\[
Q_{L L'}(k, \vec{k}') = t_{L}(k, k') \delta_{L L'} + \sum_{L_1} t_{L}(k, k') B_{L L'}^{L_1} Q_{L_1 L'}(k, \vec{k}').
\]
(2.19b)
Using the properties of the operator \( \gamma_\alpha \) developed in Appendix B, Eq. (2.15) can be recast as
\[
A(\vec{k}, E) = \lim_{E' \rightarrow 0} \left( \frac{16\pi \gamma_\alpha}{\Omega(E - k^2)^2} \sum_{L} m_{L}(E) \left| \alpha_{L}(\vec{k}, E) \right|^2 \right),
\]
(2.20)
where
\[
\alpha_{L}(\vec{k}, E) = \sum_{L} \left[ \Delta(k, k') + \Delta B_{L}(k, \vec{k}) \right] Y_{L}(\vec{k}).
\]
(2.21)
\( \Delta(k, k') \equiv t_{L}^A(k, k') - t_{L}^B(k, k') \equiv \Delta(k', k), \) and \( m_{L}(E) \) denotes the energy-shell matrix elements of the operator \( m_\alpha \). To prove \( m_{L}(E) \geq 0 \), we require a second result from Appendix B of Ref. 6:

\[
(2\pi)^{2} \delta(E - H_{0}) - G_0^2 \sum_{\delta} \gamma_\alpha (\sigma_\alpha - \sigma_\delta) G_0 \gamma_\delta P_{\alpha},
\]
(2.22)
where
\[
P_{\alpha} = \gamma_\alpha (1 - G_0 \sigma_\alpha) = \gamma_\alpha d_\alpha.
\]
(2.23)
From (2.18) it follows that \( t_{\alpha} \) satisfies the identity
\[
t_{\alpha} - t_{\alpha}^* = -(2\pi i) t_{\alpha} \delta(E - H_{0}) t_{\alpha} + (1 + t_{\alpha}^* G_0) \gamma_\alpha (\sigma_\alpha - \sigma_\delta) (1 + G_0 t_\delta).
\]
(2.24)
If the potential \( \sigma_\alpha \) were Hermitian, (2.24) would reduce to the optical theorem for \( t_{\alpha} \).] Substitution from (2.22) and (2.23) into (2.24) yields
\[
(2\pi)^{2} \delta(E - H_{0}) - G_0^2 \sum_{\delta} (2\pi)^{2} \gamma_\alpha G_0 \gamma_\delta P_{\alpha},
\]
(2.25)
and, taking energy-shell matrix elements we have
\[
\tau_{L}^* = -\kappa |\tau_{L}|^2 + \sigma L \gamma_{L} \kappa (m_{L}).
\]
(2.26)
In view of (2.12), we see that \( m_{L}(E) \) and \( M_{L}(E) \) are, in fact, equal. It follows from (2.20) that the CPA spectral function is non-negative and the link between the sign of \( A(\vec{k}, E) \) and the structure of the Argand diagram for \( \tau_{L}(E) \) is established. In deriving (2.27) from (2.25), we have again relied on results obtained in Appendix B [see Eq. (B6a)].

C. Free-electron singularities

While the preceding derivation is formally correct, it should be emphasized that several of the intermediate equations must be interpreted with care in the limit \( E^\rightarrow 0 \). For example, combining (2.16a), (2.22), and (2.23), the operator \( m_\alpha \) obeys the equations

\[
(2\pi)^{2} \gamma_\alpha \Delta_{\alpha} = -xy \Delta_{\alpha} \gamma_{\alpha} \kappa (m_{L}).
\]
(2.26)
[In deriving (2.27) from (2.25), we have again relied on results obtained in Appendix B [see Eq. (B6a)].]
m_{n} = \gamma \delta(E - H_{0}) + \sum_{q \neq a} \gamma \delta(E - H_{q}) g_{q} \gamma a + \cdots,

\rho_{m} = \gamma \delta(E - H_{0}) + \sum_{q \neq a} \gamma \delta(E - H_{q}) g_{q} \gamma a.

(2.28a)

Using the notation developed in Appendix B the energy-shell elements \{m_{L}(E)\} satisfy

\[ m_{L} = \sum_{k} \langle \bar{q} | \gamma_{k} | \alpha, L \rangle \left\{ \delta(E - q^{2}) + \sum_{q_{1} \neq 0} \langle L_{1}, \beta | q_{1} \alpha, L \rangle \right\} m_{L_{1}} N_{k}^{2} \]

(2.29a)

where

\[ \langle \bar{q} | \gamma_{k} | \alpha, L \rangle = \sum_{q_{1} \neq 0} \langle \bar{q} | \gamma_{q_{1}} \alpha, L \rangle \left\{ \delta(E - q^{2}) + \sum_{q_{1} \neq 0} \langle L_{1}, \beta | q_{1} \alpha, L \rangle \right\} \]

(2.29b)

Here \( B_{q} \) and \( f_{L} \) are defined by Eqs. (2.7) and (2.9), respectively, and the \( \bar{q} \) sum in (2.30a) again runs over just the first Brillouin zone. Note that as \( E^{*} - 0^{+} \), the magnitude of the wave vector \( \bar{q} \) in (2.30a) approaches \( \bar{q} \) because of the \( \delta \) function in (2.29)], the KKR matrix \( B_{q} \) diverges, and the contribution from the first term on the right side of (2.29) vanishes. Similarly, the singular behavior of \( B_{q} \) as \( q^{2} - E \) implies that each of the higher-order terms in (2.29b) tends to zero as \( E^{*} - 0^{+} \). We emphasize that the implication here is not that \( m_{L}(E) - 0 \), but, rather, that the physically relevant solutions of (2.29a) are not easily obtained by direct iteration. To interpret Eq. (2.29) properly, we examine in more detail the origin of these free-electron singularities.

In the derivation of Eqs. (2.15) and (2.22), the optical theorem is used to regroup the various contributions to \( \text{Im} \{ K | T(E) | \bar{K} \} \) into non-negative combinations. While the matrix element \( \langle \bar{K} | T(E) | \bar{K} \rangle \) is well behaved for all \( E \) in the upper half plane (i.e., \( E^{*} > 0 \)), certain terms that occur in this regrouping process are singular as \( E^{*} - 0^{+} \). Physically, these singular terms arise from "closed-loop" events in which an electron returns to a given site after scattering from one or more intermediate sites. They appear first in connection with the third-order terms in the multiple-scattering series. If these terms are averaged exactly, we have (suppressing angular indices)

\[ Q_{3}(k, \bar{k}) = \langle \bar{L}(k, \bar{k}) | B_{q}^{*}(\gamma) B_{q}(\gamma) \rangle \Delta(k, \bar{k}) + \text{xy} \Delta(k, \bar{k}) \left( N^{s} \sum_{q} B_{q}^{*}(\gamma) B_{q} \right) \Delta(k, \bar{k}). \]

(2.31)

The first term on the right-hand side of (2.31) is the average \( \bar{m} \)-matrix result; the second is the leading fluctuation effect retained by more sophisticated schemes like the CPA. We focus on this second contribution and in particular on the terms within the large parentheses. [Recalling (2.8) and (2.9) these terms are seen to provide the leading contribution to \( f_{L}(E) \).] Evaluating their imaginary part sequentially, we obtain

\[ \text{Im} \left( N^{s} \sum_{q} B_{q}^{*}(\gamma) B_{q} \right) = \sum_{q} \left( B_{q}^{*}(\gamma) B_{q} + B_{q}^{*}(\gamma) B_{q} + B_{q}^{*}(\gamma) B_{q}^{*} \right). \]

(2.32)

While the left-hand side of (2.32) is well behaved as \( E^{*} - 0^{+} \), it turns out that each of the three terms on the right side is singular in this limit. These singularities, of course, cancel when the three terms are added. Their presence is due to the fact that the Brillouin-zone integration on the left side of (2.32) converges only if \( E^{*} > 0 \). This is seen most easily by converting to a lattice sum:

\[ N^{s} \sum_{q} B_{q} B_{q} = \sum_{q \neq \mathbf{0}} B_{q} B_{q}, \]

(2.33a)

where

\[ B_{q} = \sum_{q \neq \mathbf{0}} e^{i \bar{q} \cdot R_{m}} B_{m}, \]

(2.33b)

As \( R = | \bar{R} - \bar{R}_{0} | \to \infty, B_{q} \) and \( B_{q} \) both vary as \( \exp(i \kappa R) \) and the right side of (2.33a) can be modeled by the integral:

\[ \sum_{q \neq \mathbf{0}} e^{i \bar{q} \cdot R_{m}} B_{m} \to \frac{1}{| \bar{R} - \bar{R}_{0} |}. \]
\[
\int_0^\infty \frac{e^{i\kappa R}}{R} R^2 dR = \frac{e^{2i\kappa R}}{2i\kappa} \left( e^{2i\kappa R} - e^{2i\kappa r_0} \right)_{r_0} \tag{2.34}
\]

where \( r_0 \) is a typical nearest-neighbor distance. Note that while the left side of (2.34) diverges if \( E'' > 0 \), a result of order unity is obtained for any \( E'' > 0 \). By contrast, if on the left side of (2.33a) we used \( B_{k=2}^{*} B_k \), as in the middle term on the right side of (2.32), we have

\[
\int_0^\infty \frac{e^{-i\kappa R}}{R} \left( e^{i\kappa R} - e^{-i\kappa R} \right)^{\infty} = \frac{e^{-2i\kappa r_0}}{2i\kappa} \tag{2.35}
\]

which diverges as \( \kappa'' \rightarrow 0 \).

Now, in the optical theorem analysis the contribution from each order in the multiple-scattering series to \( \text{Im}(\mathbf{k} \cdot [T(E) \mathbf{k}] \) is written sequentially and the resulting terms are regrupped into non-negative partial sums. In so doing, however, the singular terms encountered above will not always be grouped with their respective counterterms. This does not mean that the method is unphysical but that, if we are to obtain reasonable results, the limit \( E'' \rightarrow 0 \) must be taken after we have gone to all orders in multiple scattering. For example, on the right side of (2.29b) subsets of these singular terms have been summed in such a way that, if the limit \( E'' \rightarrow 0 \) is taken term by term the apparent solution is \( m_L = 0 \). However, if terms are first summed to all orders [as in (2.29a)], the limit \( E'' \rightarrow 0 \) does not cause any trouble. To see this in detail we note that substitution from (2.30b) into (2.29b) yields

\[
m_L = \frac{(f_k/B_k)^2}{1 + xy |\Delta J_L|^2} \left( N^{-1} \sum_q |b_q^L|^2 xy |\Delta J_L|^2 m_L \right),
\tag{2.36}
\]

where

\[
b_q^L = [1 - B_q \tau]^{-1} B_q \Delta L_L.
\tag{2.37}
\]

and \( A_L = B_L - i\kappa \). Letting \( E'' = 0 \), the renormalized structure matrix \( b_q \) varies smoothly as \( q^2 - E \) and the Brillouin-zone integration in (2.36) is clearly convergent. In the present context \( A_L \) may be treated as a real matrix in the limit \( E'' \rightarrow 0 \). For example, in the weak scattering limit \( (C''_L - xy |\Delta L|^2) \ll E^{-1} |\Delta L_L|/B_L | - 1 \) the Brillouin-zone integral of \( |b_q|^2 \) is roughly proportional to the reciprocal of a typical damping rate:

\[
N^{-1} \sum_q |b_q|^2 \sim (xy |\Delta L|^2)^{-1}
\tag{2.38}
\]

and the physically relevant solutions of (2.36) are of order unity (i.e., \( C''_L = -xy \kappa |\Delta L|^2 m_L \) is of order \( -xy |\Delta L|^2 \)).

III. ANALYSIS OF LLOYD'S REPRESENTATION OF THE CPA

Rather than constructing the spectral function \( A(k, E) \), and then integrating over all \( k \), the average density of states is more easily evaluated by employing the formalism developed by Lloyd. While Lloyd's equations are well suited to numerical implementation, they lack the symmetry of the underlying multiple-scattering theory, and thus do not provide a particularly convenient framework for discussing the formal properties of a given approximation scheme. We show in this section that, at least in the case of the CPA, the Lloyd representation can be proved to yield a non-negative spectrum. We begin with the equation

\[
\rho(E) = \langle N \rangle^{-1} \text{Im} \sum_{L,L'} \left( \frac{C_{L,L'}}{C_{L,L}} \right) \left( \frac{dC_{L',L}}{dE} - \frac{C_{L,L'} - C_{L',L}}{C_{L,L} - C_{L',L}} \right) b_{L,L'} \Delta L L' - \frac{dA_{L,L'}^{(1)}}{dE} \right| \langle C + A \rangle^{-1} \rangle_{L,L'},
\tag{3.1}
\]

which expresses the CP density of states in terms of a sum over all wave vectors \( \bar{q} \) in the first Brillouin zone, the quantities

\[
C_{A(B),L} = \kappa \cot \left( \delta A(B)^{(1)}(E) \right)
\tag{3.2}
\]

and

\[
A_L = -\kappa L + i \kappa,
\tag{3.3}
\]

and we again define \( A_q = B_q - i \kappa \). To simplify our analysis, angular indices will again be suppressed. Denoting the spherical Bessel and Neumann functions as \( f_j(x) \) and \( n_j(x) \), we introduce the following diagonal matrices:

\[
J_j^2 = [j_j(x \kappa)]^2, \quad \kappa n_j = \kappa f_j(x \kappa) n_j(x \kappa) \delta_{L,L'},
\tag{3.4a}
\]

\[
C'_{A(B)} = C_{A(B)} - \kappa j n / j^2
\tag{3.4b}
\]

and

\[
v_{A(B)} = \kappa \delta A(B)^{(1)}(E) - \gamma_0(E),
\tag{3.4c}
\]
where \( \gamma_{A(B)} \) and \( \gamma_0(E) \) are, respectively, the logarithmic derivatives of the \( A(B) \) and free-electron radial wave functions at the muffin-tin radius \( \gamma_{m} \). The identity
\[
\frac{d}{dE} \left( j^2 C_{A(B)} \right) = \frac{d}{dE} \left( \kappa_j \nu \right) + \left( j^2 C'_{A(B)} \right) \frac{d \nu_{A(B)}}{dE}
\]
(3.5)
is then easily established and (3.1) can be rewritten as
\[
\rho(E) = (N\pi)^{-1} \text{Im} \sum_{\mathbf{q}} \text{Tr} \left( \frac{C - C_{B}}{C_{A}} \right) \frac{d \nu_{A}}{dE} - \left( \frac{C - C_{B}}{C_{A}} \right) \frac{d \nu_{B}}{dE} \left( \frac{dP_{\mathbf{q}}}{dE} \right) \left( j(C + A_{\mathbf{q}}) j \right)^{-1},
\]
(3.6)
where \( P_{\mathbf{q}} \) is given by (3.1), the identity (3.6) and the trace operation refers to the implicit angular indices. The energy derivative of the matrix \( P_{\mathbf{q}} \) can be written as an integral over a single Wigner-Seitz cell (volume \( \Omega_{\mathbf{q}} \))
\[
- \frac{dP_{\mathbf{q}}}{dE} = \int_{\Omega_{\mathbf{q}}} P_{\mathbf{q}}(\mathbf{r}, \mathbf{L}) P_{\mathbf{q}}(\mathbf{L}', \mathbf{L}) d^3 \mathbf{r},
\]
(3.7)
where
\[
P_{\mathbf{q}}(\mathbf{r}, \mathbf{L}) = (\Omega_{\mathbf{q}})^{-1} \sum_{\mathbf{r}'} e^{i \mathbf{r} \cdot \mathbf{r}'} j_1 \left( \frac{\mathbf{r} + \mathbf{r}'}{\mathbf{r} \cdot \mathbf{r}'} \right) \frac{\nu_{\mathbf{q}}(\mathbf{r} + \mathbf{r}')}}{E - \left( \mathbf{k} + \mathbf{r} \right)^2}
\]
(3.8)
Now, let the integration in (3.7) be divided into (1) the region within the muffin-tin sphere and (2) the interstitial region between the sphere and the boundary of the Wigner-Seitz cell. Using the identity
\[
\frac{dy}{dE} = \left( \nu_{\mathbf{q}} j \right)^2 \sum_{\mathbf{r}} \nu^2 \left( \nu_{\mathbf{q}} j \right)^2 d\mathbf{r},
\]
(3.9)
the first of these contributions can be put in the form
\[
\left( \frac{dP_{\mathbf{q}}}{dE} \right) = \left( \nu_{\mathbf{q}} j \right)^2 \left( A_{\mathbf{q}} + \frac{\kappa_{\mathbf{q}}}{j} \right) \left( \nu_{\mathbf{q}} j \right)^2 \frac{dy}{dE}.
\]
(3.10)
Recalling (3.4c), we see that the terms in (3.6) involving \( d \nu_{A}/dE \) and \( d \nu_{B}/dE \) also give rise to contributions proportional to \( d \nu_{C}/dE \). Combining these with (3.10), one component of \( \rho(E) \) is
\[
\rho_{1}(E) = (N\pi)^{-1} \text{Im} \sum_{\mathbf{q}} \text{Tr} \left( \frac{C_{A} + C_{B}}{C_{A}} \right) \left( C_{A} C_{B} - A_{\mathbf{q}}^2 \right) \left( C + A_{\mathbf{q}} \right) \left( \nu_{\mathbf{q}} j \right) \left. \frac{dy}{dE} \right|_{\mathbf{q}}.
\]
(3.11)
The sign of the terms in the large parentheses on the right side of (3.11) is not explicitly constrained. Nevertheless, when the Brillouin-zone sum is carried out, it can easily be seen that \( \rho_{1}(E) \) vanishes. We emphasize, however, that this result depends on the fact that \( C \) in (3.11) is the CP effective cotangent. Indeed, introducing the diagonal matrix
\[
T_{C} = -N^{-1} \sum_{\mathbf{q}} \left( C + A_{\mathbf{q}} \right)^{-1},
\]
(3.12)
the CPA equation may be written as\(^{11,12}\)
\[
\left( \nu_{\mathbf{q}} j \right)^2 \left( A_{\mathbf{q}} + \frac{\kappa_{\mathbf{q}}}{j} \right) \left( \nu_{\mathbf{q}} j \right)^2 \frac{dy}{dE}.
\]
We consider next, contributions to (3.6) arising from the interstitial region of integration in (3.7):
\[
\rho_{2}(E) = -(N\pi)^{-1} \sum_{\mathbf{q}} \sum_{\mathbf{q}'} \text{Im} \int_{\Omega_{\mathbf{q}}} P_{\mathbf{q}}(\mathbf{r}, \mathbf{L}) P_{\mathbf{q}}(\mathbf{L}', \mathbf{L}) d^3 \mathbf{r} \left( C + A_{\mathbf{q}} \right) \left( \nu_{\mathbf{q}} j \right) \frac{dy}{dE}.
\]
(3.14)
Using the inversion symmetry of the lattice and recalling the definitions (3.8), the integration over the interstitial region yields a result that is purely real and can be expressed as
\[
\int_{\Omega_{\mathbf{q}}} P_{\mathbf{q}}(\mathbf{r}, \mathbf{L}) P_{\mathbf{q}}(\mathbf{L}', \mathbf{L}) d^3 \mathbf{r} = \int_{\Omega_{\mathbf{q}}} \sum_{\mathbf{k}} \left[ \cos(\mathbf{k} \cdot \mathbf{r}) \cos(\mathbf{k} \cdot \mathbf{r}') + \sin(\mathbf{k} \cdot \mathbf{r}) \sin(\mathbf{k} \cdot \mathbf{r}') \right] P_{\mathbf{q}}(\mathbf{r}) P_{\mathbf{q}}(\mathbf{r}') d^3 \mathbf{r}.
\]
(3.15)
where
\[ P_\xi(L, n) = \frac{1}{\xi_0 j_1(\xi r_n)} j_1(\xi r_n) P_\xi(\xi r_n) \left( \frac{E - (\xi + \frac{1}{2} K)^{\xi}}{E - \frac{1}{2} K^2} \right)^{-\gamma}. \] (3.16)

Contributions to the imaginary part of the term in large parentheses in (3.14) are then due entirely to the inverse matrix \((C + A)^{-1} = K\). The identity
\[ \text{Im}[(C + A)^{-1}] = \sum_{\xi L_1} K_{L_1 L}^* C_{L_1 L} K_{L_1 L'} \] (3.17)
together with (3.15) then implies that \(\rho_s(E)\) can be expressed as a sum of non-negative terms
\[ \rho_s(E) = -(N\pi)^{-1} \sum_{\xi L_1} C_{L_1 L} \int_{(1/2)} d^3q \chi_{\xi}^* \chi_{\xi} \chi_{\xi}^* \chi_{\xi} \] (3.18)
where
\[ \chi_{\xi}^* = \chi_{\xi} = \frac{1}{\xi_0 j_1(\xi r_n)} j_1(\xi r_n) P_\xi(\xi r_n) \] (3.19a)
and
\[ \chi_{\xi}^* = \chi_{\xi} = \frac{1}{\xi_0 j_1(\xi r_n)} j_1(\xi r_n) P_\xi(\xi r_n). \] (3.19b)

Note that we have fixed the sign of \(\rho_s(E)\) using only the fact \(\xi^2 > 0\).

Finally, we consider the contributions to (3.6) proportional \(dy_A/\xi dE\) and \(dy_A/\xi dE\):
\[ \rho_s(E) = -\pi^{\xi} \text{Im} \left[ \text{Tr} \left( \frac{\partial \chi_{\xi}^* \chi_{\xi}}{\partial \xi} \right) \right]. \] (3.20)

[The Brillouin-zone sum in (3.6) has been executed via (3.12).] Given the CPA condition (3.13), Eq. (3.20) is easily rewritten as
\[ \rho_s(E) = \pi^{\xi} \text{Im} \left[ \text{Tr} \left( \frac{x(r_n) C_A^2 \partial y_A}{\xi E} \left( \frac{T_\infty}{1 + (C - C_A)^T_\infty} \right) \right) \right]. \] (3.21)

In (3.21), only the quantities in large parentheses have nonvanishing imaginary parts. Using again the fact that \(T_\infty\) and \(C\) are related by (3.13), these are
\[ \text{Im} \left[ \text{Tr} \left( \frac{T_\infty}{1 + (C - C_A)^T_\infty} \right) \right] = \frac{y(x) C''}{x(y)(C_A - C)^2}. \] (3.22)

Since \(C'' < 0\) and \(dy_A/\xi dE < 0\), we have
\[ \rho_s(E) = \pi^{\xi} \text{Tr} \left( \frac{y(r_n) C_A^2 \partial y_A + x(r_n) C_A^2 \partial y_A}{C_A - C} \right) \geq 0, \] (3.23)
and the proof is complete.

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APPENDIX A: DERIVATION OF Eqs. (2.6)

For a given \(E' = E + i\kappa\), the total scattering operator \(T\) and its Hermitian conjugate \(T^\dagger\) satisfy the optical theorem
\[ T - T^\dagger = -2\pi i T^\dagger \delta(E - H_0) T. \] (A1)

Equations (2.3), (2.4), and (A1) then allow \(A(\mathbf{k}, E)\) to be written as
\[ A(\mathbf{k}, E) = \delta(E - k^2) [1 + \mathbf{k}^2] G_0(k) + G_0(k)^2 \mathbf{k}^2 [\mathbf{k}^2 | \mathbf{k}^2] + | G_0(k) |^2 \sum_n | \mathbf{k} + \mathbf{k}_n | T | \mathbf{k}_n |^2 | \delta(E - (\mathbf{k} + \mathbf{k}_n)^2) \] (A2)
where \(G_0(k) = (E' - k^2)^{-1}\) and \(\mathbf{k}_n\) is a vector of the reciprocal lattice. The first four terms on the right-hand side of (A2) contribute only at the free-electron singularities \(k^2 = E\) and \((\mathbf{k} + \mathbf{k}_n)^2 = E\). To show that these singular contributions cancel exactly, we recall that the evaluation of both \(\mathbf{k}^2 \mathbf{G} \mathbf{k}\) and \((\mathbf{k} + \mathbf{k}_n)^2 \mathbf{G}(\mathbf{k} + \mathbf{k}_n)^2\) involves the inverse matrix \((1 - \tau B_\xi)^{-1}\) and that the structure functions \(B_\xi\) are singular as \((\mathbf{k} + \mathbf{k}_n)^2 = E\) (for any \(\mathbf{k}_n\)). The following limits are then easily established:
\[ \lim_{k^2 \rightarrow E} | G_0(k) |^2 | \mathbf{k} + \mathbf{k}_n | T | \mathbf{k}_n |^2 | \delta(E - (\mathbf{k} + \mathbf{k}_n)^2) | = \delta_{n,0} \delta(E - k^2) \] (A3a)
\[ \lim_{k^2 \rightarrow E} \left[ | G_0(k) |^2 | \mathbf{k} + \mathbf{k}_n | T | \mathbf{k}_n |^2 | \delta(E - (\mathbf{k} + \mathbf{k}_n)^2) | \right] = \delta_{n,0} \delta(E - k^2) \] (A3b)
and, for \( n \neq 0 \)
\[
\lim_{\mathbf{k} \to \mathbf{K}_n} \left[ |G_o(k)|^2 \left| \mathbf{k} + \mathbf{K}_n \right|^T \left| \mathbf{k} - \mathbf{K}_n \right|^2 \delta(E - \mathbf{k} + \mathbf{K}_n)^2 \right] = 0.
\]
\[\text{(A3c)}\]

[On the left sides of (A3b) and (A3c), \( \delta(k) \) should be understood as \( \pi^{-1} \epsilon_1/(x^2 + \epsilon_2) \) and the limit \( \epsilon \to 0^+ \) is to be taken after the limits \( k^2 - E \) and \( (\mathbf{k} + \mathbf{K})^2 - E \).] Substituting from (A3) into (A2) we have

\[
A(\mathbf{k}, E) = |G_o(k)|^2 \left| \mathbf{k} \right|^T \left[ \left( \mathbf{T} \delta(E - H_o) \mathbf{T} \right) - \left( \mathbf{T} \delta(E - H_o) \mathbf{T} \right) \left| \mathbf{k} \right|^2 \right],
\]
which is equivalent to (2.1).

**APPENDIX B: PROPERTIES OF THE OPERATOR \( \gamma_a \)**

Equation (2.17) defines \( Q_a \) in terms of the scattering path operator \( Q_{a,a'} \). Similarly we now define

\[
Q_a^T = \sum_{a'} Q_{a,a'},
\]
where \( (T) \) indicates the transpose operation. \( Q_{a}, \) \( Q_{a}^T, \) and \( \sigma_a \) are related by

\[
Q_a (1 + G_o T)^{-1} = \sigma_a = (1 + T G_o)^{-1} Q_{a}^T.
\]

Substituting from the above equations into the definition (2.16), \( \gamma_a \) is easily written as

\[
\gamma_a = (1 + T G_o) \left( 1 - \left[ (\tau \omega) + (y - x) \Delta_a \right] G_o \sum_{b \neq a} Q_{b} G_o + Q_{a} G_o \right)^{-1}
\]
\[\text{(B2)}\]

\[
= \left( 1 + \sum_{b \neq a} Q_{b} G_o \right) \left( 1 - \left[ (y - x) \Delta_a - xy \Delta_a + \Delta_a \Delta_a \right] G_o \sum_{b \neq a} Q_{b} G_o (1 + t_o G_o)^{-1} \right)^{-1},
\]
\[\text{(B3)}\]

where, in (B3) we have used the operator version of Eq. (2.8).\(^{20}\) Equations (2.3) and (2.4) can be combined to rewrite one component of the inverse operator in (B3) in a more symmetric form:

\[
G_o \sum_{b \neq a} Q_{b} G_o (1 + t_o G_o)^{-1} = G_o \sum_{b \neq a, \gamma \neq a} \gamma_{a} G_o.
\]
\[\text{(B4)}\]

Similarly, a combination of operators appearing in (2.30b) can be rearranged as follows:

\[
(1 + G_o f)^{-1} G_o \left( 1 + \sum_{b \neq a} Q_{b} G_o \right) = G_o + G_o \sum_{\gamma \neq a, b \neq a} \gamma_{a} G_o.
\]
\[\text{(B5)}\]

We now show how Eqs. (B3), (B4), and (B5) simplify the evaluation of the quantity \( m_L \). These equations, together with the fact that the operator \( m_a \) is always acted on by \( \Delta_a \) from both the right and left [c.f., Eqs. (2.15) and (2.26)], imply that only the energy-shell matrix elements of \( m_a \) are required for the evaluation of the CPA spectral density. We argue that on the right-hand sides of (2.15) and (2.26) \( m_a \) can, in effect, be represented by the operator\(^{21}\)

\[
m_a = \frac{k}{\pi} \int \, d\tau \, d^2 \tau' \left| \tau > j_1(\kappa |\tau - \bar{R}_a)| Y_L(\bar{R} - \bar{R}_a) m_L Y_L(\bar{R}' - \bar{R}_a) j_1(\kappa |\bar{R}' - \bar{R}_a|) < \bar{R}' \right|
\]
\[\text{(B6a)}\]

\[
= \frac{k}{\pi} \sum_{L} \left| \alpha, L > N \right| \, m_L N_1 < L, \alpha \mid,
\]
\[\text{(B6b)}\]

where

\[
\frac{k}{\pi} \int \, d\tau \, d^2 \tau' \left| \tau > j_1(\kappa |\tau - \bar{R}_a)| Y_L(\bar{R} - \bar{R}_a) m_L Y_L(\bar{R}' - \bar{R}_a) j_1(\kappa |\bar{R}' - \bar{R}_a|) < \bar{R}' \right|
\]
\[\text{(B7)}\]

\[
= \int \, \langle L, \alpha | \bar{R} | m_a | \bar{R} ' \rangle Y_L(\bar{R} - \bar{R}_a) \langle \bar{R}' | j_1(\kappa |\bar{R}' - \bar{R}_a|) Y_L(\bar{R}' - \bar{R}_a) j_1(\kappa |\bar{R} - \bar{R}_a|) < \bar{R}' \rangle \, d\tau \, d^2 \tau',
\]
\[\text{(B8a)}\]

\[
= \int \, \langle L, \alpha | \bar{R} | m_a | \bar{R} ' \rangle Y_L(\bar{R} - \bar{R}_a) \langle \bar{R}' | j_1(\kappa |\bar{R}' - \bar{R}_a|) Y_L(\bar{R}' - \bar{R}_a) j_1(\kappa |\bar{R} - \bar{R}_a|) < \bar{R}' \rangle \, d\tau \, d^2 \tau',
\]
\[\text{(B8b)}\]

and

\[
N_1 = \int \, r^2 \, j_1^2(\kappa r) \, dr.
\]
\[\text{(B8c)}\]

Recalling (2.16), we see that, if \( \gamma_a \) could be replaced by the unit operator, Eqs. (B7) and (B8) would follow immediately from the representations.
\[ \langle \Phi | (E - H_0) | \Phi' \rangle = \kappa \tau^{-1} \sum_{\lambda} Y_{\lambda}(\Phi) j_\lambda(kr) j_\lambda(kr') Y_{\lambda}(\Phi'), \]  
(B9a)

and (for \( \beta \neq \alpha \))

\[ \langle \Phi - R_{\alpha} | G_0 | \Phi - R_{\alpha} \rangle = \sum_{\lambda \lambda'} Y_{\lambda}(\Phi) j_\lambda(kr) B_{\alpha \lambda}^{LL'} j_{\lambda'}(kr') Y_{\lambda'}(\Phi'), \]  
(B9b)

where \( B_{\alpha \lambda} \) is defined by Eq. (2.33). Substituting from (B4) into (B3) we see that the higher-order contributions to \( \gamma_\alpha \) are such that when \( \gamma_\alpha \) acts on \( \Delta_\alpha \) from the left, the coupling always takes place via terms of the form \( t_\alpha G_0 \Delta_\alpha \), where \( n \neq \alpha \). Equation (B9b) then guarantees that only energy-shell matrix elements are involved in the coupling of \( \gamma_\alpha \) and \( \Delta_\alpha \). (Similar remarks apply for the combination \( \Delta_\alpha \gamma_\alpha \).) Consider next the evaluation of \( m_L \) via Eq. (B7). The relevant matrix elements of (B4) and (B5) are

\[ \langle L, \alpha | G_0 \sum_{\beta \neq \alpha \gamma \alpha} Q_\beta G_0 | \alpha, L' \rangle = N^{-1} \sum_q b_q^{LL} c_B, \]

(B10a)

and

\[ (1 - \delta_{\alpha \beta}) \langle L, \beta | G_0 + \sum_{\gamma \neq \alpha \gamma \alpha} Q_\gamma G_0 | \alpha, L' \rangle = (1 - \delta_{\alpha \beta}) \left( B_{\alpha \beta} + \sum_{\gamma \neq \alpha \gamma \alpha} B_{\alpha \gamma} \gamma^T \gamma_{\alpha \beta} \right) LL'. \]

(B10b)

Substituting from (B10) and (2.9) into (B3), Eqs. (2.30) are easily derived, and \( m_L \) is then determined by the renormalized equation (2.29a).

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13Without providing any formal proof, various authors have speculated on the validity of the results established in Sec. II B c.f. Sec. III.3 of Ref. 11 and III of the first paper cited in Ref. 12.
16It follows from (2.10) that \( m_L \rightarrow 1 \) in the ATA, and, therefore, that \( C'_L \) is again negative.
17In the limit \( E'' \rightarrow 0^+ \), the first term on the right side of (2.29a) does indeed vanish.
18It should be emphasized that (2.36) is not a homogeneous equation in \( m_L \). While \( \{ m_L \} = 0 \) is a solution of (2.36), the dependence of \( b_q \) on \( \{ m_L \} \) via (2.37) implies that this trivial solution is not stable.
20It can be proved that the off-shell matrix elements of the effective CPA scattering operator may be written as

\[ t_L(k, k') = \phi_L(k, k') + \Delta_L(k, k')f_L(n)\Delta_L(k, k). \]

The derivation of this result and a discussion of its implications for the CPA spectral density will be discussed in a forthcoming publication.
21In Eqs. (B6) and (B8), the conventions have been so chosen that in the ATA, \( m_{\alpha} = \delta(E - H_0) \) and \( m_L = 1 \).